# Infrared absorption spectrum of pentafluorophenol

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(*Received 8 March 1977, revised 19 April 1977*)

The infrared absorption spectrum of pentafluorophenol in the liquid state has been recorded on a Perkin Elmer model 521 grating spectrophotometer in the region 4000–250 cm$^{-1}$. Assuming $C_{2v}$ symmetry for the molecule, observed bands have been analysed in terms of fundamental frequencies and their combinations. Fundamentals corresponding to all the allowed modes of vibration of the molecule have been identified and correlated on the basis of their intensity and magnitude in other similar molecules.

## 1. INTRODUCTION

Ferguson *et al* (1953), Tripathi *et al* (1975) and Green *et al* (1971) have reported infrared spectra of a large number of mono-, di-, tri- and tetra-substituted fluoro derivatives of benzene, aniline and phenol, and pentafluoroaniline and bromo-benzene. Rai *et al* (1969) have studied the infrared spectra of pentafluoro toluene and anisole. Recently, absorption spectrum of pentafluorophenol (PFP hereafter referred) has been studied by Singh *et al* (1973). A search of literature, however, reveals that no Raman or infrared spectra have been reported for this molecule as yet. The present paper deals with a study of the infrared spectrum and assignment of the vibrational frequencies to all the allowed modes of PFP molecule. Mooney (1968) has pointed out that in polyfluorinated aromatics the nature of the substituent often causes severe perturbation of the aromatic ring vibrations. This point is further supported by our observations in this molecule.

## 2. EXPERIMENTAL

The sample of PFP was obtained from Koch Light Ltd., England and was used without further purification. The infrared absorption traces of the compound in the liquid state were taken on a double beam Perkin Elmer 521 grating spectrophotometer in the region 4000–250 cm$^{-1}$. The frequencies measured at peak absorptions are accurate to $\pm 10$ cm$^{-1}$. The spectrum of PFP molecule has been analysed in terms of fundamentals and their combinations by assuming approximate symmetry $C_{2v}$ taking OH group as one unit, and with the two-fold axis the $Z$-axis and $X$-axis perpendicular to the plane of the molecule. Thus 30 normal vibrations can be divided into various symmetry species as $11a_1 + 10b_2$

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(planar) and $3a_1 + 6b_1$ (nonplanar). Except for the $a_2$ modes, which are inactive in the infrared, all the other modes are allowed. Assignments of all the fundamentals corresponding to allowed modes have been given in the table.

Two ranges of absorption for phenols are observed at 3250–3200 cm$^{-1}$ and 3617–3593 cm$^{-1}$ in the bonded and unbonded states respectively (Bellamy 1959, Colthup 1975). While the frequency appearing in the latter range as a sharp band has been assigned as free hydroxyl (OH) stretching vibration, that in the former appearing as a very broad but more intense band has been interpreted as hydroxyl stretching vibration when intermolecular bonding exists as expected in liquids or solids (Bellamy 1959). Due to intramolecular chelation in alcohols and phenols frequencies in the range 3200–2500 cm$^{-1}$ are expected to appear (Bellamy 1959). In the infrared spectrum of the present molecule we observe three bands in the above regions at 3582, 3340–3145 and 2666 cm$^{-1}$ possessing usual characteristics and therefore have been assigned to free hydroxyl intermolecular bonded hydroxyl and intramolecular chelated hydroxyl stretching vibrations respectively in conformity with the assignments of previous workers.

Two doubly degenerate C–C vibrations $e_{2g}$ (1596 cm$^{-1}$) and $e_{1u}$ (1485 cm$^{-1}$) of benzene split into four distinct vibrations under the reduced symmetry of substituted benzenes. The two compounds corresponding to the first of these vibrations of benzene are observed in the region 1620–1500 cm$^{-1}$ in mono-, di-, and polysubstituted benzenes while the compounds of second vibration are observed in these molecules in the region 1500–1400 cm$^{-1}$. In the present case, however, we observe four very strong bands in a comparatively narrow region 1535–1510 cm$^{-1}$ and these have been correlated with four components of the above vibrations of benzene. There is no strong band around 1600 cm$^{-1}$ which could be correlated with the higher component of $e_{2g}$ vibration of benzene. On the other hand we have a band of medium intensity at 1480 cm$^{-1}$ which could be correlated with the lower component of $e_{1u}$ vibration of benzene. But we have preferred to describe it as the $a_1$ C–F stretching vibration in view of its ability to combine with other fundamentals to explain many bands in the spectrum. Another C–C vibration in pentafluorobenzenes Tripathi et al 1975, Rai et al 1969) corresponding to $b_{2u}$ (1310 cm$^{-1}$) vibration of benzene has been assigned at about 1350 cm$^{-1}$ by previous workers. We have correlated a strong band at 1345 cm$^{-1}$ to this mode.

Other prominent bands in this region are expected to appear corresponding to the C–F stretching, C–O stretching and O–H in plane deformation modes. All these bands could be taken as fundamentals and assigned to the above modes in conformity with the correlations in similar molecules (Green et al 1972). The shifts observed in the ring frequencies from their usual magnitudes are most probably due to the perturbation of the ring by the nature of the substituent as observed by Mooney (1968).

Table 1.  Fundamental frequencies of pentaflusrophend

| Position (cm$^{-1}$) | Intensity | Symmetry | Approximate description of the mode of vibration |
|---|---|---|---|
| 251 | m | $b_1$ | $\phi(C-F)$ |
| 310 | m(sh) | $b_1$ | $\phi(C-F)$ |
| 321 | w(sh) | $b_1$ | $\phi(C-O)$ |
| 340 | vvw | $b_1$ | $\phi(C-F)$ |
| 350 | vw | $b_1$ | $\phi(C-F)$ |
| 370 | w | | $\phi(O-H)$ |
| 380 | vw | $b_2$ | $\beta(C-F)$ |
| 392 | vw | $b_1$ | $\phi(C-C)$ |
| 440 | mw | $a_1$ | $\beta(C-C-C)$ |
| 468 | vvw | $b_2$ | $\beta(C-O)$ |
| 551 | mw | $b_2$ | $\beta(C-C-C)$ |
| 595 | vvw | $b_2$ | $\beta(C-F)$ |
| 608 | w | $a_1$ | $\beta(C-F)$ |
| 645 | w | $b_2$ | $\beta(C-F)$ |
| 665 | w | $a_1$ | $\beta(C-F)$ |
| 780 | m | $a_1$ | $\nu(C-C)$ ring breathing |
| 972 | vvs | $b_2$ | $\nu(C-F)$ |
| 990 | vvs | $a_1$ | $\beta(C-C-C)$ trigonal mode |
| 1015 | vvs | $a_1$ | $\nu(C-F)$ |
| 1130 | ms | $b_2$ | $\nu(C-F)$ |
| 1150 | w | | $\beta(O-H)$ |
| 1230 | s | $a_1$ | $\nu(C-O)$ |
| 1305 | s | $a_1$ | $\nu(C-F)$ |
| 1345 | s | $b_1$ | $\nu(C-C)$ |
| 1480 | m | $a_1$ | $\nu(C-C)$ |
| 1510 | vvs | $b_2$ | $\nu(C-F)$ |
| 1515 | vvs(sho) | $a_1$ | $\nu(C-C)$ |
| 1530 | vvs | $a_1$ | $\nu(C-C)$ |
| 1535 | vvs(sho) | $b_1$ | $\nu(C-C)$ |
| 2666 | vw(b) | — | $\nu(O-H)$ Intermolecular-Chelation |
| 3145 | ms(vb) | | |
| 3190 | m(vb) | | $\nu(O-H)$ Intermolecular bonded |
| 3340 | m(vb) | | |
| 3582 | m | — | $\nu(O-H)$ free |

$\nu$ = stretching, $\beta$ = i.p. bending, y — o.p. bending, vvs = very very strong, vs = very strong, s = strong, ms = medium strong, w = weak, mw = medium weak, vvw — very very weak, sho = shoulder, vb = very broad, sh = sharp.

Pitzer & Scott (1943) have pointed out that $a_{1g}$ (995 cm$^{-1}$) ring breathing and $b_{1u}$ (1010 cm$^{-1}$) C–C–C deformation vibrations of benzene combine in mono-, meta- and 1,3,5 trisubstituted benzenes to give rise to two triagonal modes in one of which 1,3,5 carbon atoms move and in the other only those at 2,4 and 6 move. While the latter takes exactly the average value of the two frequencies, the former is reduced in magnitude. Kovner & Bogomolov (1961) and Fateley et al (1968) have correlated the former with the mode $b_{1u}$ and the latter with the mode $a_{1g}$ of benzene. The present molecule is quite similar in geometry to a monosubstituted benzene except for the fact that we have here $F$ atoms in place of the five $H$ atoms of benzene ring. Thus this type of mixing can be expected in the present case also. In view of this we have correlated a very strong frequency at 990 cm$^{-1}$ and another frequency of medium intensity at 780 cm$^{-1}$ to $b_{1u}$ and $a_{1g}$ modes of benzene respectively.

In the frequency range below 700 cm$^{-1}$ we have been able to identify fundamentals corresponding to all the deformation C–F, C–O, O–H (Torsion) and C–C–C modes. While both the components corresponding to $e_{2g}$ (608 cm$^{-1}$) vibration of benzene have been observed with almost equal intensity at 551 and 440 cm$^{-1}$, only one weak band corresponding to $e_{2u}$ (404 cm$^{-1}$) has been taken at 392 cm$^{-1}$, as the other component is forbidden in the infrared, in conformity with previous workers (Tripathi et al 1975). The O–H out of plane deformation (torsional) frequency has been assigned at 370 cm$^{-1}$ which compares fairly well with the observations of Green et al (1972).

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